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Synthesis of Cross-Conjugated Dibenzochrysene-Based Photosensitizers for Dye-Sensitized Solar Cells

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SYNTHESIS OF CROSS-CONJUGATED DIBENZOCHRYSENE-BASED
PHOTOSENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

by
Bailey Nicole Flamm

A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2017

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ABSTRACT

Dye-sensitized solar cells (DSCs) represent a promising alternative method of energy generation. Absorbance of light across the visible spectrum and into the near-infrared (NIR) region is crucial to increasing the power conversion efficiencies (PCEs) of DSC devices. Dye absorbance can be red-shifted by either increasing the conjugation path of the photosensitizer or by increasing the strength of electron donors and acceptors found in molecules. By using a polycyclic aromatic π -bridge in a dye, lower energy wavelengths of light can be absorbed. Dibenzochrysene is a six-ring polycyclic aromatic hydrocarbon (PAH) with substitutable positions that allow for a double-donor, double-acceptor (DD- π -AA) structure, in which both donors and both acceptors contribute to the electronic properties of the structure. This under-utilized dye structure benefits from the additive electron donation strength provided by two donor groups, allowing for a narrowed optical band gap and deeper absorbance into the NIR region. Additionally, the usage of two anchoring groups creates dye molecules that bind tightly to metal oxide semiconductors and leads to more stable solar devices. To date, several synthetic strategies have been attempted towards the creation of these types of dyes.

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Introduction.

The importance of energy for sustaining the current lifestyle of citizens in the United States is unparalleled, especially compared to the 20th century.¹ Energy is utilized in every aspect of life—from modes of transportation to talking on a cellphone—placing it at the forefront of modern human life. Energy supports the advancement of scientific discoveries, from instruments used in the identification of molecules, to the instrumentation researchers use to perform the syntheses of those molecules.² Sources of energy must always be present for this current lifestyle to be maintained.

As of 2015, 90% of the energy used in the United States is derived from nonrenewable energy resources.³ More than one-third of the total energy consumed comes from the use of oil, with transportation being a major contributor to oil consumption.⁴ In order to utilize a reliable energy source, the availability of that particular source needs to be assessed. The production of oil in the United States is not paralleled to the consumption, with the disparity between production and consumption increasing over time up to 2008.⁵ Currently, the U.S. must rely on oil imports due to the diminished domestic oil production and inability to meet consumption demands, with many of the oil sources being located in Africa and the Middle East.⁶ It would be far better for the U.S. to attain self-sufficiency in regard to its energy consumption.

An option for self-sustainability is to use solar energy that is provided to earth every day—energy that is being wasted because a cheap, efficient way to harvest the energy has yet to be accomplished.⁷ The sun provides the earth with enough solar energy to greatly exceed the energy needs of the world. The energy need for the world by 2050 is projected to be 28 terawatts (TW).⁸ Although 1.7×10^5 TW of solar energy is provided to

the earth each day, 600 TW are potentially available for realistic use due to spatial constraints.⁸ With this available energy, solar cells having only 10% efficiency could provide enough energy for the world.⁸ Development of efficient photovoltaic technologies to convert solar energy to electricity can allow for energy production at a cost competitive with traditional non-renewable sources. Crystalline silicon-based solar cells have experienced prolific use over the years due to their high efficiency. However, use of Si-based cells also incurs high monetary costs due to intensive manufacturing conditions. Dye-sensitized solar cells (DSCs) provide the potential for an efficient, rugged, and affordable way to harvest the energy of the sun.⁸

Dye-sensitized solar cells work by converting photons to electricity using a photosensitizer absorbed to the surface of a metal oxide semiconductor, most commonly TiO_2 (**Figure 1**).

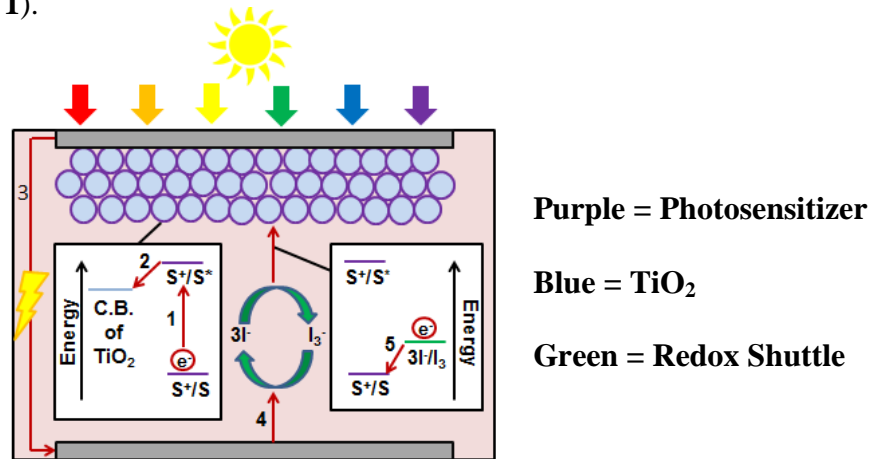


Figure 1. Basic operating principles of a DSC.

The sensitizer is promoted to an excited-state through the absorption of photons (1). The excited dye then injects an electron into the conduction band of the semiconductor (2). The electron will continue through a circuit from the TiO_2 to the counter-electrode (3), after which a redox shuttle will carry the electron to the oxidized

dye molecule (4 and 5).⁸ Only photons with the proper amount of energy will excite an electron in the ground-state to the excited-state. Increasing the number of photons a sensitizer can absorb by red-shifting the dye's absorbance can have a tremendous impact on the amount of photocurrent a device can generate (**Figure 2**).

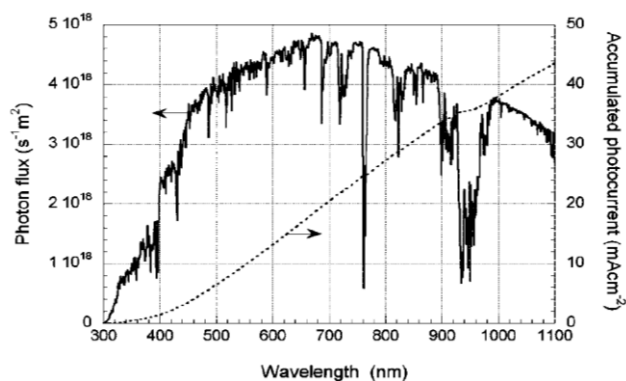


Figure 2. Photon flux of the solar spectrum along with accumulated photocurrent. Reprinted with permission from A. Hagfeldt, et al., *Chem. Rev.*, **2010**, *110*, 6595. Copyright © 2010 American Chemical Society.

The power conversion efficiency (PCE) of a DSC to convert photons to electrical energy can be shown by the following **Equation 1**⁸:

$$\eta \text{ (PCE)} = (V_{oc} \times J_{sc} \times FF)/I_0$$

V_{oc} = open circuit voltage

J_{sc} = short circuit current density

FF = fill factor

I_0 = intensity of sunlight

Equation 1. Equation used to calculate the power conversion efficiency of DSC devices.

Increasing the photocurrent density (J_{sc}) was the primary interest in this project due to its near linear relationship with photon absorption. As the current increases in a DSC device, the overall efficiency increases as the current and efficiency are directly proportional.⁸ Dye energy levels can be tuned through the use of stronger donor and

acceptor moieties. Narrowing the optical band gap (E_g^{opt}) of a dye allows for excitation of dye molecules using lower energy photons. As the energy gap between the ground- and excited-state of the dye decreases, the required energy of photons for excitation also decreases, increasing the number of photons available for excitation. A dibenzochrysene-based cross-conjugated photosensitizer was utilized in this project, with the ability to tune two donor and two acceptor groups for the desired bathochromic shift.

Typical dye design follows the ubiquitous D- π -A structure (D = donor, A = acceptor).⁸ Using this structure, tuning of energy levels relies solely on increasing charge transfer ability with a single donor and single acceptor subunit. However, using a cross-conjugated π -bridge allows for the summation of electron donation or accepting ability. To this end, we endeavored to synthesize a cross-conjugated dye using a dibenzochrysene π -bridge (**Figure 3**).

The basis of the target dye was to have a π -bridge connected to two electron donating groups and two electron accepting groups (DD- π -bridge-AA). This model was used to design the target dye with a dibenzochrysene π -bridge, being both polycyclic and aromatic.

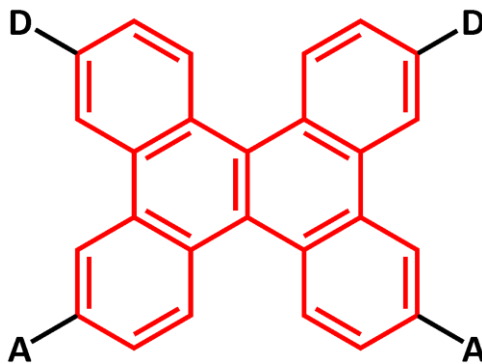


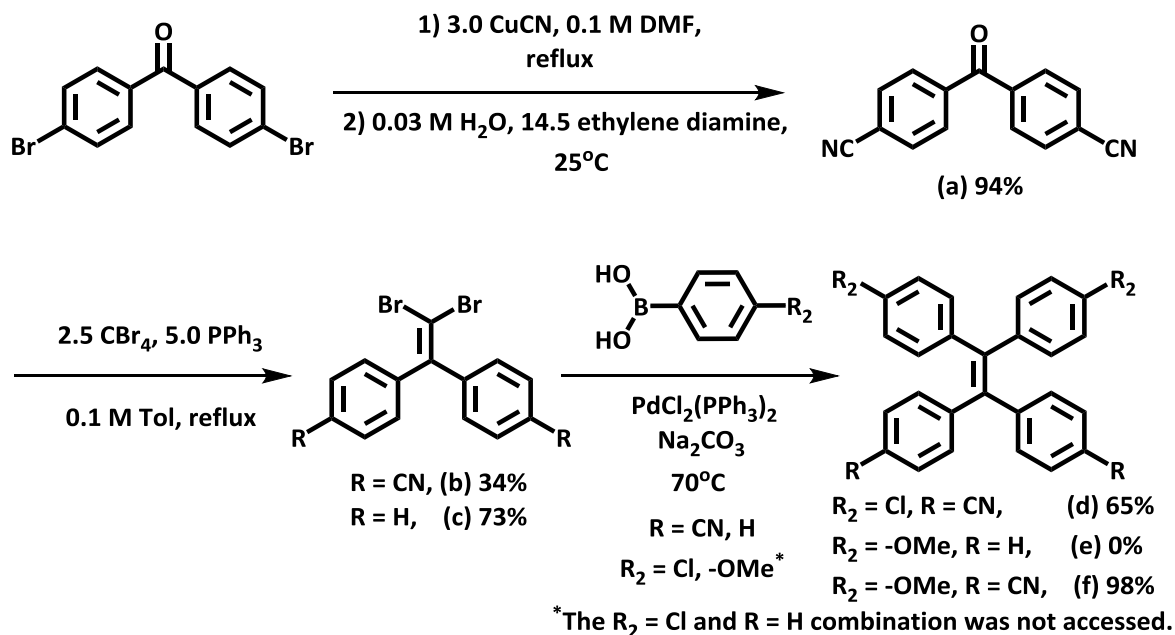
Figure 3. General structure of a dibenzochrysene-based dye using two donors (D) and two acceptors (A).

The cross-conjugated system allows for the optical band gap to be minimized, due to a higher energy ground-state and lower energy excited-state compared to a less conjugated system. Instead of one donor and one acceptor, a dibenzochrysene contains substitutable positions allowing for the ability to place two donor groups on the dye, as well as two acceptors. Tuning energy levels by incorporating stronger donors and stronger acceptors will also decrease the energy gap between the ground- and excited-states of the dye. This diminished energy gap will allow the dye to absorb in the NIR region of the electromagnetic spectrum, achieving the purpose of this project to absorb a greater number of photons to increase the current in the DSC.

The double acceptor groups allow for stronger binding on the TiO_2 surface and greater device stability as well as two sites for electron injection. The cross-conjugated dibenzochrysene π -bridge provides a conjugated π -system for electrons to travel from either donor to either acceptor. These characteristics of a dibenzochrysene-based photosensitizer make it a good candidate for synthesis.

Results and Discussion.

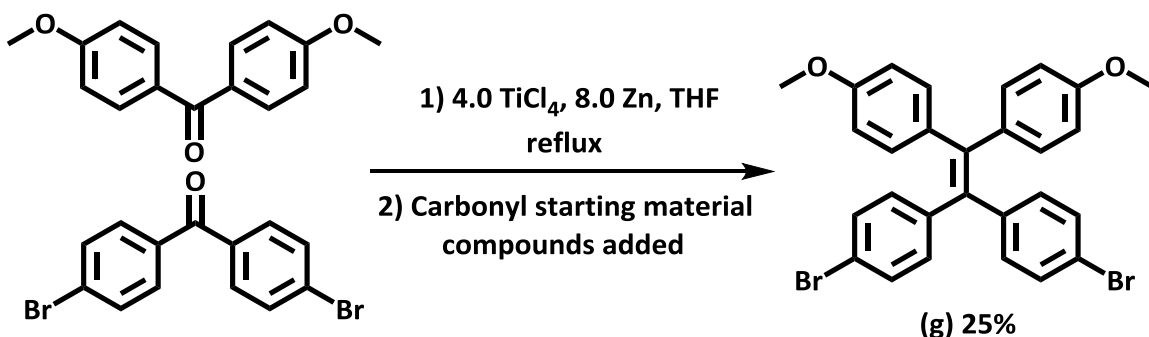
A key tetra-substituted alkene intermediate was synthesized using two different routes: a Suzuki cross-coupling route (**Scheme 1**) and a McMurry coupling route (**Scheme 2**).



Scheme 1. Suzuki cross-coupling-based route to the tetra-substituted alkene.

A cyanation reaction was performed to efficiently convert the bromine groups on the 4,4'-dibromobenzophenone to nitrile groups. A partial Corey-Fuchs reaction to synthesize **(b)** from the 4,4'-dicyanobenzophenone **(a)** produced a poor yield of 34%. This can be attributed to the poor solubility of the precursor ketone. Intermediate **(b)** was then sent through a Suzuki coupling to form the tetra-substituted alkene **(d)** with an obtained yield of 65%. Intermediate **(f)** was synthesized in a separate Suzuki coupling with 4-methoxyphenylboronic acid with a yield of 98%. In an attempt to increase the yield of the partial Corey-Fuchs reaction, benzophenone was used in place of **(a)** to obtain a yield of 73% of **(c)**. The Suzuki reaction to couple **(c)** to methoxyphenyl groups

did not produce the intended tetra-substituted alkene (**e**) as discovered using ^1H NMR.



Scheme 2. Tetra-substituted alkene achieved in a single step using a McMurry coupling.

The McMurry Coupling was assessed as a more expedient route to the tetra-substituted alkene. 4,4'-dibromobenzophenone was used in place of 4,4'-dicyanobenzophenone to ensure adequate solubility, and 4,4'-dimethoxybenzophenone was used instead of 4,4'-dichlorobenzophenone. The anisole-substituted alkene was targeted in an effort to increase electron density in the conjugated system and thereby acquire a material more suitable for oxidative cyclizations. The target product 4,4'-(2,2-bis(4-bromophenyl)ethene-1,1-diyl)bis(methoxybenzene) (**g**) was synthesized along with the homocoupled products 1,1,2,2-tetrakis(4-bromophenyl)ethene and 1,1,2,2-tetrakis(4-methoxyphenyl)ethene, as judged by the ^1H NMR of the crude product mixture. Fortunately, each product was easily separated through the use of column chromatography. Intermediate (**g**) allows for the specific substitution of double donor and double acceptor groups at their respective positions. This provides specificity in future reactions for the bromine groups to be converted to tunable acceptors, and the methoxy groups in the donor positions provide the opportunity to substitute with tunable donors. The homocoupled products would lack the specificity needed for the conversion of these groups to their specific roles. All three products were synthesized, as discovered by ^1H

NMR, which accounts for the low percent yield of the target product of 25%. This percent yield proved to be the greater percent yield to obtain the tetra-substituted product, as opposed to the overall 14% yield from the three-step process presented in **Scheme 1**.

A proposed mechanism for the McMurry coupling shows how radicals are formed from the carbonyl precursors by the use of low valent titanium to produce the desired alkene product (**Figure 4**).

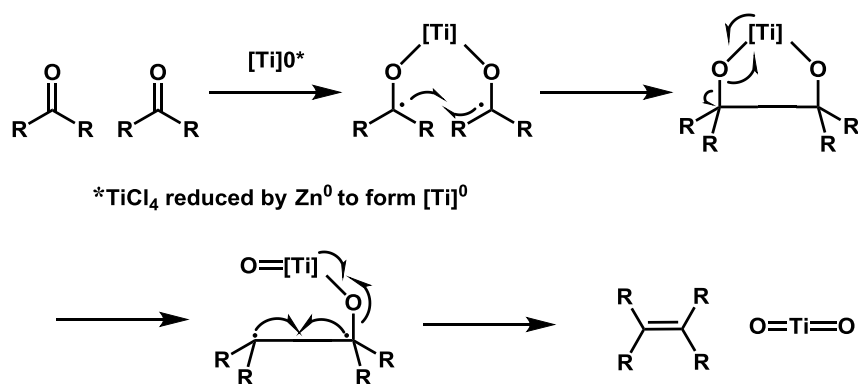
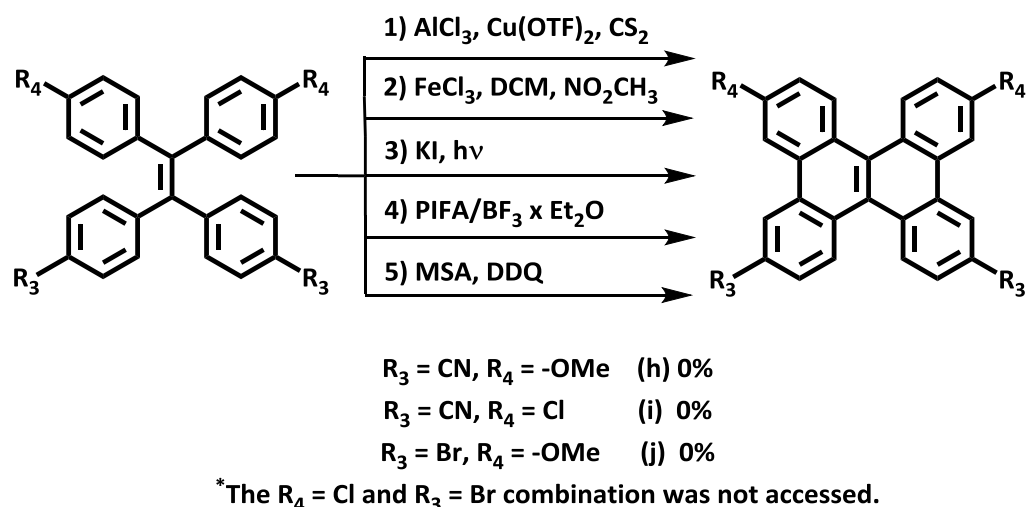


Figure 4. Proposed McMurry coupling mechanism.⁹

The tetra-substituted alkene intermediates from both the palladium cross-coupling reactions and the McMurry coupling were subjected to various oxidative cyclization conditions in pursuit of the dibenzochrysene π -bridge.



Scheme 3. Five types of oxidative reactions attempted to access the dibenzochrysene.

The tetra-substituted alkene intermediates from both the palladium cross-coupling and McMurry coupling were used as the starting material for the oxidative cyclization reactions. Each number, 1-5, represents a different oxidation reaction that was attempted on the tetra-substituted alkenes. The tetra-substituted alkenes had different groups attached to the donor and acceptor positions as represented by the various R groups shown. The first and second oxidation reactions shown depict Scholl-type reactions with the separate use of aluminum(III) chloride (AlCl_3) and iron(III) chloride (FeCl_3). The third oxidation shown depicts a light-induced oxidation with potassium iodide. The fourth oxidation uses phenyliodine(III) bis(trifluoroacetate) (PIFA), a hypervalent iodine species, with boron trifluoride in diethyl ether. The fifth oxidation route uses methanesulfonic acid (MSA) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). ^1H NMR data revealed that (f) and (g) produced mono-cyclized products (k) and (l) from the light induced cyclization in quantitative yields, and (g) produced a mono-cyclized product (m) from the oxidation reaction using MSA and DDQ, as shown in **Figure 5**.

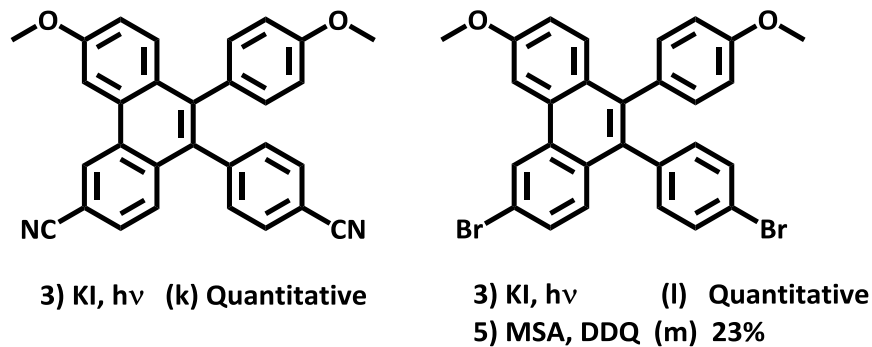
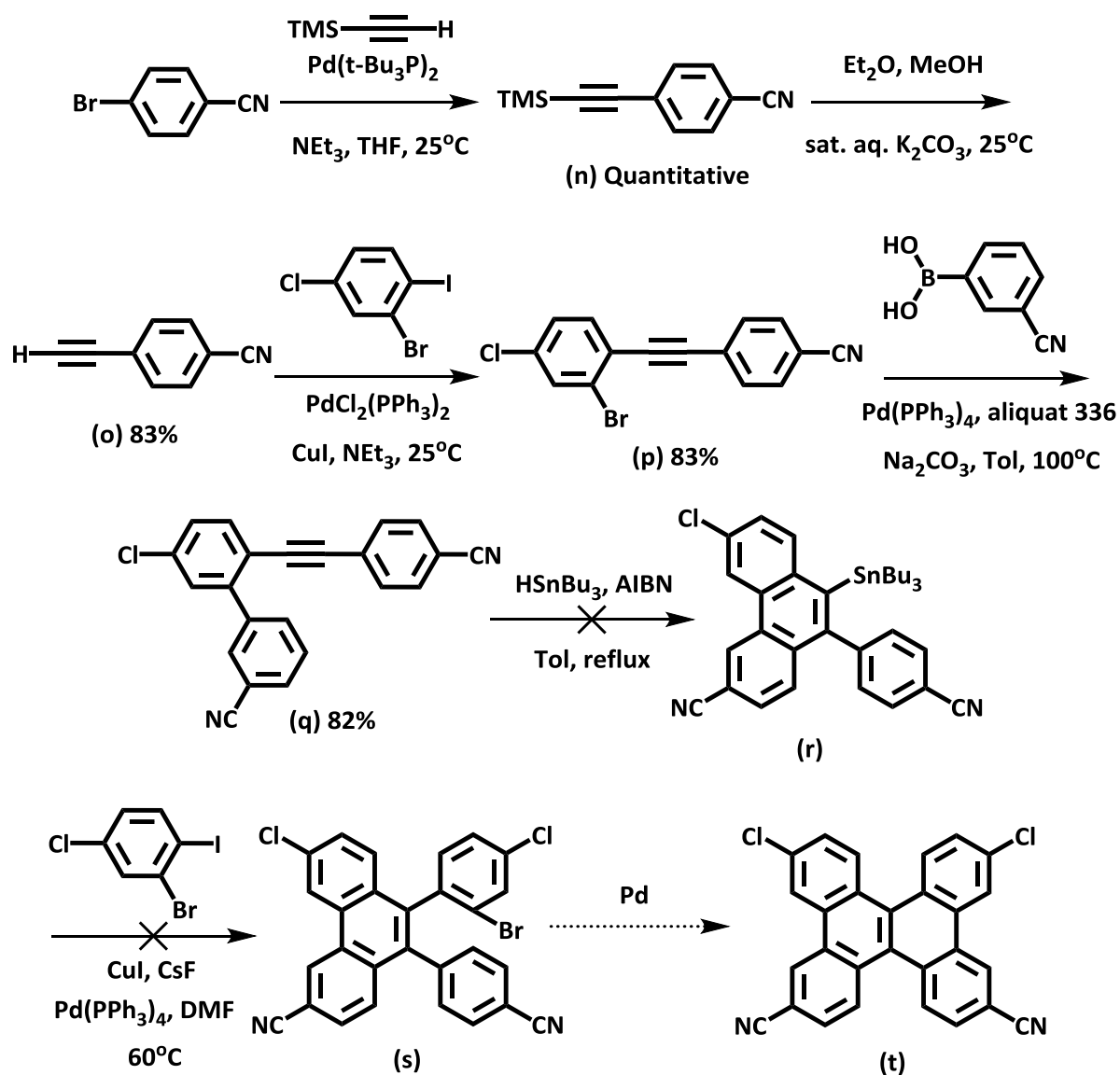


Figure 5. The mono-cyclized products from oxidation routes (3) and (5).

The mono-cyclized product (**k**) was subjected to separate reactions utilizing the first, second, and fourth oxidative cyclization conditions in an attempt to synthesize the di-cyclized product. Unfortunately, no dibenzochrysene was observed by ^1H NMR using any of these routes.

A radical tin cyclization was also assessed, shown in **Scheme 4**.



Scheme 4. Radical tin cyclization based route to dibenzochrysene intermediate.

The radical tin cyclization was attempted as an alternate route to form the dibenzochrysene dye. The reaction scheme provided promising yields for the first steps of the synthesis. The Sonogashira coupling produced the desired TMS-protected alkyne in quantitative yields. Subsequently, the deprotected alkyne was acquired in a yield of 83% under aqueous basic conditions. This was followed by a Sonogashira coupling

reaction to couple 2-bromo-4-chloro-1-iodobenzene to (**o**) to produce (**p**) with a yield of 83%. The Sonogashira coupling was followed by a Suzuki coupling reaction to obtain (**q**) by coupling (3-cyanophenyl)boronic acid to (**p**) with a yield of 82%. A radical tin cyclization was attempted on the alkyl precursor (**q**); however, interpretation of the crude ^1H NMR was unclear. The crude material was carried forward without purification as Sn-based compounds are frequently unstable to silica columns frequently used for flash chromatography. The Stille cross-coupling reaction was then attempted despite the unclear ^1H NMR spectrum under the assumption of the potential presence of (**r**). Unfortunately, the desired product of the Stille coupling was not produced, concluding that the intended product of the tin cyclization reaction most likely had not been produced in the previous reaction.

The palladium cross-coupling reactions, along with the McMurry reaction produced their intended products, but could not be continued after the oxidative reactions were deemed unsuccessful upon review of ^1H NMR spectra from the products of the reactions. Contributing factors in the failure of these reactions compared to the literature procedures potentially stems from different functional groups in the donor and acceptor positions compared to the molecules used in these reactions.

Conclusion.

This project to synthesize a dibenzochrysene photosensitizer with two donors and two acceptors was not successful. The failure of the syntheses stemmed from difficulties related to cyclization of intermediates using either oxidative cyclization conditions or a radical tin-based cyclization route. The benefits of utilizing a dibenzochrysene group as a π -bridge in a photosensitizer, including higher current density values to increase the efficiency of DSCs as well as two acceptors for stability on the surface of the semiconductor, should not be overlooked. The future of this project could include different synthetic schemes that do not rely on the ring-closing oxidations that were assessed in this project, and pursue an entirely different route to form the dibenzochrysene π -bridge. Other groups attached to the dibenzochrysene could be analyzed for success in the oxidation reactions as the literature reactions were successful and the syntheses performed in this project were unsuccessful. Although the target of the project was unable to be produced, the reactions completed provides for a successful beginning on gathering information for the future projects handling dibenzochrysene-based photosensitizers.

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Supplemental Information

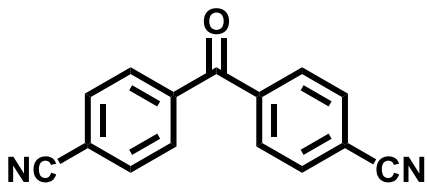
Experimental: Synthesis

General Information

Commercially obtained reagents and extra dry solvents were used as received. All reactions were performed under a N₂ atmosphere unless otherwise noted. Thin-layer chromatography (TLC) was conducted with Sorbent Technologies, Inc. glass backed 250 μ m Silica Gel XHL TLC plates with UV254 indicator and visualized with UV. Flash column chromatography for intermediates was performed with Sorbent Technologies, Inc. silica gel, porosity 60 Å, 40-63 μ m. ¹H NMR spectra were recorded on a Bruker Avance-300 (300MHz) spectrometer and a Bruker Avance-500 (500MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent, dd = doublet of doublets; coupling constant(s) in Hz; integration.

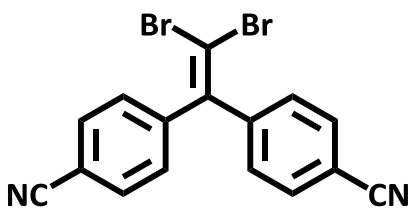
Experimental for Scheme 1:

4,4'-carbonyldibenzonitrile (a)¹⁰ -



4,4'- dibromobenzophenone (1.00 g, 2.94 mmol) was placed into a round-bottomed flask along with copper(I) cyanide (CuCN) (0.79 g, 8.82 mmol) and a stir bar. The flask was then pump cycled, and 98 mL of degassed DMF were added to the flask with the use of a cannula. The reaction mixture was then placed under reflux at 160 °C for 48 hours and monitored using thin layer chromatography (TLC). This reaction mixture was then diluted with H₂O, and filtered to collect the solid crude product. This crude product was then suspended in H₂O and stirred with N, N'-dimethylethylenediamine (4.57 mL) at room temperature for 1 hour. This mixture was washed with H₂O, then filtered to obtain the solid product; 94%. ¹H NMR (300 MHz): δ 7.92-7.69 (m, 8H).

4,4'-(2,2-dibromoethene-1,1-diyl)dibenzonitrile (b)¹¹ -

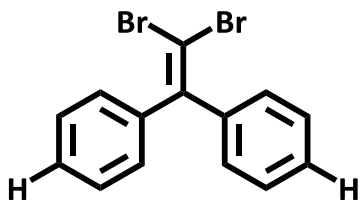


Intermediate (a) (0.11 g, 0.45 mmol) was placed into flame dried round bottomed flask and dissolved in dry toluene (4.5 mL, 0.1 M), along with triphenylphosphine (PPh₃) (0.6 g, 2.25 mmol) and carbon tetrabromide (CBr₄) (0.4 g, 1.13 mmol). The reaction was placed under reflux at 130 °C for 12 hours, and was monitored by TLC and ¹H NMR. The reaction mixture was degassed, and another equivalent each of PPh₃ and CBr₄ were added after the reaction showed no progress, with only starting material present. The reaction was placed back under reflux for 12 hours. After determining there was no starting material present, the reaction

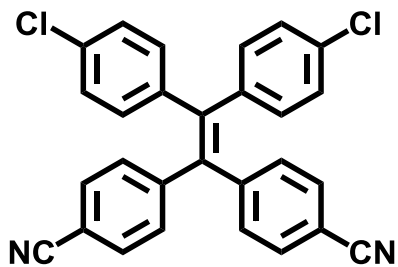
mixture was diluted with DCM and sent through a plug with DCM. The product was columned in 75% DCM:Hx to produce a yellow-brown product; 34%. ^1H NMR (500 MHz): δ 7.67 (d, J = 8.3 Hz, 4H), 7.41 (d, J = 8.3 Hz, 4H).

(2,2-dibromoethene-1,1-diyl)dibenzene (c) -

Synthesized according to literature.¹²

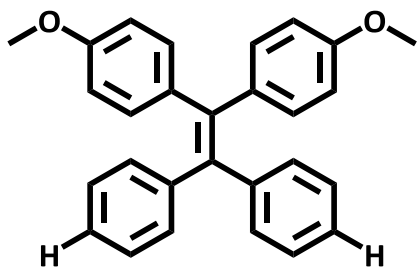


4,4'-(2,2-bis(4-chlorophenyl)ethene-1,1-diyl)dibenzonitrile (d)¹³ -



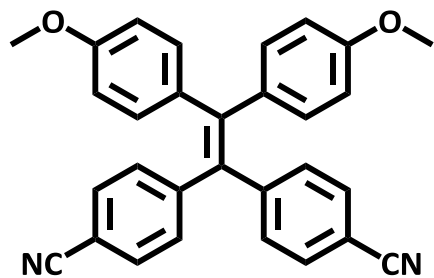
Intermediate **(b)** (0.04 g, 0.09 mmol) was dissolved in 4:1 mixture (1.6 mL: 0.4 mL) of THF and water. 4-chlorophenylboronic acid (0.05 g, 0.32 mmol) and Na_2CO_3 (0.03 g, 0.28 mmol) were then added to the same flask. The reaction mixture was degassed for 15 minutes before $\text{PdCl}_2(\text{PPh}_3)_2$ (0.01 g, 0.01 mmol) was added. The reaction was heated at 70 °C for 48 hours, and was monitored using TLC and ^1H NMR. The reaction was extracted with DCM and water, and dried with Na_2SO_4 . A plug was performed using 25% DCM:Hx. The product was a light yellow oil; 65%. ^1H NMR (300 MHz): δ 7.46 (d, J = 8.2 Hz, 4H), 7.15 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.1 Hz, 4H), 6.91 (d, J = 8.4 Hz, 4H).

4,4'-(2,2-diphenylethene-1,1-diyl) bis (methoxybenzene) (e)¹³ -



Synthesis attempted in the same manner as (d), however (c) was used as a starting material, and 4-methoxyphenylboronic acid was used as the coupling partner. Analysis of ¹H NMR showed miniscule amount of product and starting material compared to a high concentration of an unknown product that inhibited further use of (e).

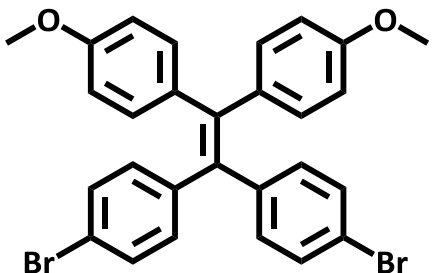
4,4'-(2,2-bis(4-methoxyphenyl)ethene-1,1-diyl) dibenzonitrile (f)¹³ -



Synthesis attempted in the same manner as (d), however, 4-methoxyphenylboronic acid was used in place of 4-chlorophenylboronic acid. Yield: 98%. ¹H NMR (300 MHz): δ 7.41 (d, J=8.1 Hz, 4H), 7.09 (d, J=8.1 Hz, 4H), 6.90 (d, J=8.4 Hz, 4H), 6.68 (d, J=8.4 Hz, 4H).

Scheme 2:

4,4'-(2,2-bis(4-bromophenyl)ethene-1,1-diyl) bis(methoxybenzene) (g) -



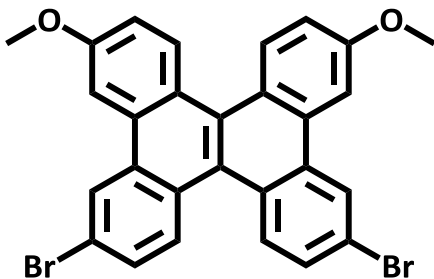
Synthesized according to literature.¹⁴

Scheme 3:

Five oxidation routes were attempted in an effort to synthesize the dibenzochrysene π -bridge. Not all five oxidation reactions were attempted to obtain each (h), (i), and (j), however, each attempted product is listing according to the oxidation route attempted. Only one synthesis is provided for each attempted product, as the conditions used were similar for each starting material.

Oxidation Route (1) AlCl_3 , $\text{Cu}(\text{OTf})_2$, CS_2 : Attempted for (h) and (j).¹⁵

2,7-dibromo-10,15-dimethoxydibenzo[g,p]chrysene (j) – Intermediate (g) was



dissolved in dry dichloromethane (DCM) (121 mL).

Carbon disulfide (CS_2) (9.1 mL) was then added, and the reaction mixture was degassed for 20 minutes.

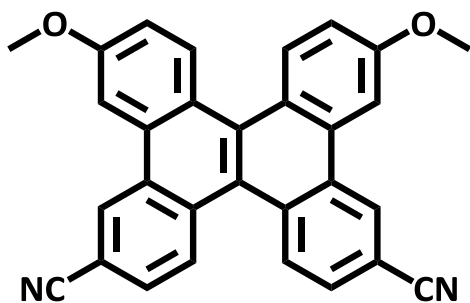
While this reaction mixture was degassing, AlCl_3 (0.1 g, 0.73 mmol) was added to a flame-dried flask with

copper(II) triflate [$\text{Cu}(\text{OTf})_2$] (0.33 g, 0.91 mmol) and dissolved in dry DCM (15 mL).

The first reaction mixture was cooled to 0 °C, and the second reaction mixture was added dropwise. The reaction was allowed to warm to room temperature overnight, and was monitored by TLC. Starting material was still present after 24 hours, therefore the reaction was then placed under reflux at 40 °C after the addition of 1 equivalent each of AlCl_3 and CS_2 . The reaction was allowed to proceed overnight. Analysis of the TLC showed only starting material still present, therefore reaction was deemed unsuccessful.

Oxidation Route (2) FeCl_3 , DCM, NO_2CH_3 : Attempted for (h).¹⁶

10,15-dimethoxydibenzo[g,p]chrysene-2,7-dicarbonitrile (h) – Intermediate (f) (0.05

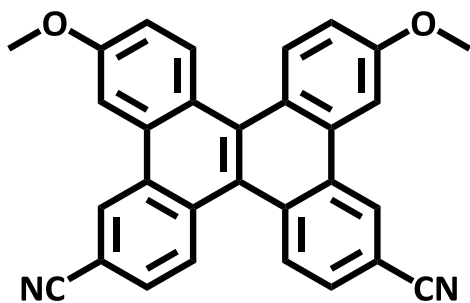


g, 0.1 mmol) was added to a flame dried flask and dissolved in dry DCM (2 mL). In a separate flame dried flask, FeCl_3 (0.07 g, 0.4 mmol) was dissolved in nitromethane (CH_3NO_2) (0.3 mL), and added to the reaction mixture dropwise. The

flask was then purged with N_2 , and left to stir at room temperature for 40 minutes. The reaction was monitored using TLC, and after 40 minutes, starting material was still present. After 72 hours, the DCM in the reaction was blown off with N_2 , and replaced with DCE (2 mL). The reaction flask was then placed under reflux at 80 °C and left to run overnight. The reaction was checked both by TLC and ^1H NMR, and determined to be unsuccessful due to both lack of starting material, and expected product.

Oxidation Route (3) KI , $h\nu$: Attempted for (h) and (j).¹⁷

10,15-dimethoxydibenzo[g,p]chrysene-2,7-dicarbonitrile (h) -



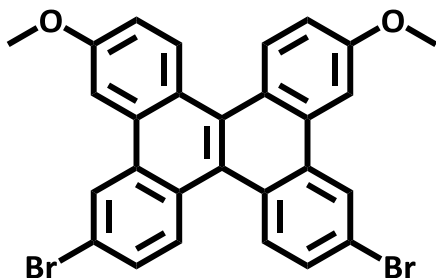
Intermediate (f) (0.05 g, 0.1 mmol) was combined with potassium iodide (KI) (0.2 g, 1.11 mmol) and dissolved in cyclohexane (111 mL, 0.001 M). This mixture was evenly dispersed between two 56 mL pyrex phototubes. The tubes were then

taped together and hung by a wire into the photoreactor for 5 hour. The reaction was monitored using ^1H NMR, which showed starting material was still present and

monocyclized product present. Iodine (I_2) was added to one reaction tube and 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) (0.18 g, 1.12 mmol) was added to the other tube. Both tubes were placed back in the photoreactor for 12 hours. 1H NMR revealed only monocyclized product. The reaction mixture with I_2 was extracted with DCM and water, and dried with sodium sulfate (Na_2SO_4). The monocyclized product was then reacted under both **Oxidation Route (2)** and **Oxidation Route (3)** conditions, separately, in an effort to create the desired dibenzochrysene. These reactions were determined to be unsuccessful in providing the expected product.

Oxidation Route (4) PIFA/ $BF_3 \times Et_2O$: Attempted on (h) and (j).¹⁸

2,7-dibromo-10,15-dimethoxydibenzo[g,p]chrysene (j):



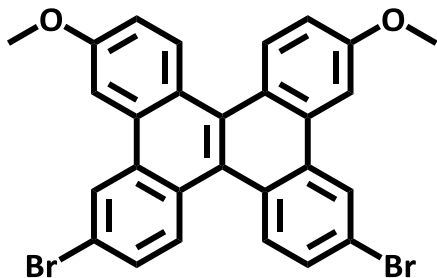
Intermediate (g) (0.1 g, 0.18 mmol) was added to a round bottomed flask and dissolved in dry DCM (3.8 mL, 0.048 M). Phenyliodine(III) bis(trifluoroacetate) (PIFA) (0.39 g, 0.91 mmol) and boron trifluoride (BF_3) in diethyl ether (Et_2O) (0.13

mL) were dissolved in dry DCM (3.8 mL, 0.048 M) in a separate flask. This mixture was then added to the first reaction mixture dropwise at $-60\text{ }^{\circ}C$. This reaction was allowed to run for 1 hour before being warmed to $0\text{ }^{\circ}C$. After 12 hours, the purple reaction mixture was checked by both TLC and 1H NMR. The reaction was deemed to be incomplete and was stirred for 12 hours. After the 12 hours, the reaction was then extracted with DCM and water, and dried with Na_2SO_4 . The crude 1H NMR showed no starting material present, as well as an unknown product. The reaction was deemed unsuccessful in

providing the expected product.

Oxidation Route 5) MSA, DDQ: Attempted for products (i) and (j).¹⁹

2,7-dibromo-10,15-dimethoxydibenzo[g,p]chrysene (j):

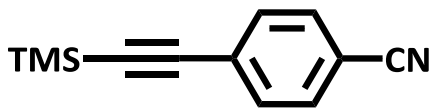


Intermediate (g) (0.1 g, 0.2 mmol) was dissolved in dry DCM (7.4 mL), and cooled to 0 °C. Methanesulfonic acid (MSA) (0.8 mL) and DDQ (0.04 g, 0.2 mmol) were added to the flask, and the reaction mixture turned a dark purple. The reaction

was monitored by TLC and ¹H NMR. After 12 hours starting material was still present, therefore more DDQ (0.01 g, 0.04 mmol) was added in an effort to push the reaction forward. After 18 hours, the reaction was extracted with DCM and H₂O, and dried with Na₂SO₄. The starting material was absent, however, the peaks in the ¹H NMR did not correspond to the intended product. The reaction was determined to be unsuccessful in providing the expected product.

Scheme 4.

4-((trimethylsilyl)ethynyl)benzonitrile (n)²⁰:

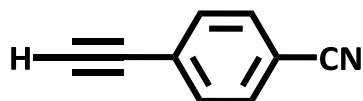


4-bromobenzonitrile (1 g, 5.48 mmol), trimethylsilylacetylene (3.78 mL), tetrahydrofuran (THF) (5.5 mL), and triethylamine (5.5 mL) were

added to a flame dried flask. Pd(t-Bu₃P)₂ (0.07 g) was then added, and the reaction stirred at room temperature for 12 hours. Reaction was monitored by TLC and ¹H NMR which showed the starting material was absent, and the reaction was extracted with DCM and

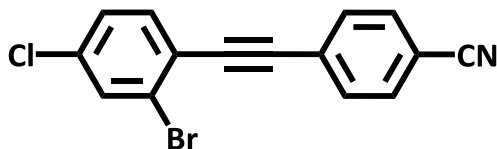
H₂O, and dried with Na₂SO₄. The crude product was then sent through a plug with 5% DCM:Hx for a quantitative yield. ¹H NMR (300 MHz): δ 7.60 (d, J=8.4 Hz, 2H), 7.54 (d, J= 8.6 Hz, 2H).

4-ethynylbenzonitrile (o)¹⁹:



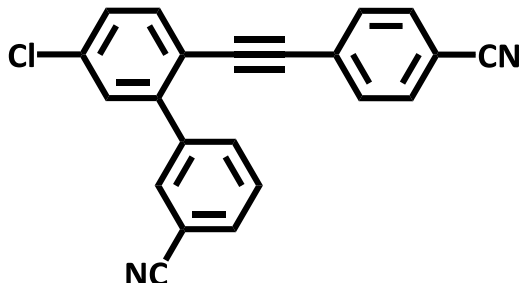
Intermediate (**n**) (0.5 g, 2.51 mmol), Et₂O (2.5 mL), methanol (MeOH) (10 mL), and saturated potassium carbonate (K₂CO₃) (10 mL) were added to a round bottomed flask open to air and stirred vigorously for 7 hours. The reaction mixture was extracted with Et₂O and H₂O, and dried with Na₂SO₄. The crude product was run through a plug with 60% DCM:Hx to produce a white solid; 83%. ¹H NMR (300 MHz): δ 7.64 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3, 2H), 3.30 (s, 1H).

4-((2-bromo-4-chlorophenyl)ethynyl)benzonitrile (p)²¹:



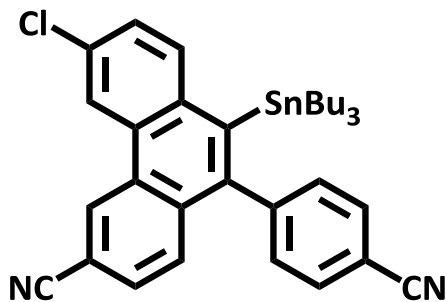
2-bromo-4-chloro-1-iodobenzene (0.22 g, 1.18 mmol), PdCl₂(PPh₃)₂ (0.015 g, 0.04 mmol), copper(I) iodide (CuI) (0.007 g, 0.06 mmol), and triethylamine (12 mL) were added to a flame dried flask. In a separate flask, (**o**) was pump cycled and dissolved in triethylamine (12 mL). The alkyne solution was added slowly to the first flask, and stirred at room temperature for 12 hours. Reaction was monitored by TLC and ¹H NMR which showed that there was no more starting material. The reaction was extracted with Et₂O and saturated aqueous ammonium chloride (NH₄Cl), and dried with Na₂SO₄. The crude product was run through a column with 40% DCM:Hx, to produce the white powder product; 83%. ¹H NMR (300 MHz): δ 7.88 (d, J=6.5 Hz, 2H), 7.82 (d, J=2 Hz, 1H), 7.81 (d, J=8.5 Hz, 2H), 7.71 (d, J=8.4 Hz, 1H), 7.54

5'-chloro-2'-((4-cyanophenyl)ethynyl)-[1,1'-biphenyl]-3-carbonitrile (q)²²:



mixture, a drop of aliquat 336 (*N*-methyl-*N,N,N*-triethylammonium chloride) was added, and the reaction mixture was degassed for 15 minutes. Pd(PPh₃)₄ (0.007 g, 0.006 mmol) was added to this flask, and the reaction was heated to 100 °C for 12 hours. The reaction was monitored by TLC and ¹H NMR, and after starting material was no longer present, the reaction was extracted with DCM and H₂O, and dried with Na₂SO₄. The crude product was sent through a plug with 75% DCM:Hx to isolate the product; 82%. ¹H NMR (500 MHz): δ 7.96 (s, 1H), 7.83 (d, J=7.9 Hz, 1H), 7.74 (d, J=7.8 Hz, 1H), 7.62 (d, J=7.5 Hz, 2H), 7.59 (d, J=6.7 Hz, 2H), 7.43 (d, J=1.9 Hz, 1H), 7.42 (dd, J=2.15 Hz, 8.2 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H).

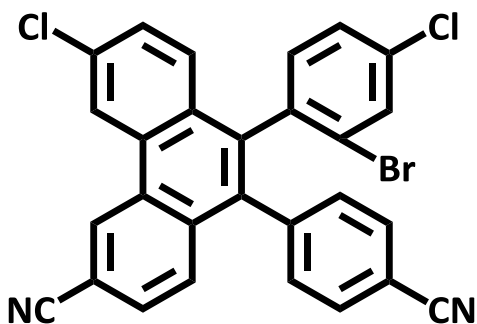
6-chloro-10-(4-cyanophenyl)-9-(tributylstannyl)phenanthrene-3-carbonitrile (r)¹⁹:



25

then added to the first flask and refluxed at 140 °C for 12 hours. Consumption of starting material was monitored by TLC and ^1H NMR which showed starting material was still present. 0.5 equivalents of AIBN and HSnBu_3 , along with 1 mL of toluene were added to the reaction mixture and allowed to run for 24 hours. The reaction was filtered with a celite pad, and the solvent was evaporated using a rotary evaporator. The ^1H NMR spectrum presented multiple peaks, with lack of starting material peaks. Isolated peaks of the product were unable to be identified, therefore the product was carried forward under the assumption the intended product was present in the conglomeration of peaks.

9-(2-bromo-4-chlorophenyl)-6-chloro-10-(4-cyanophenyl)phenanthrene-3-carbonitrile (s)²³:

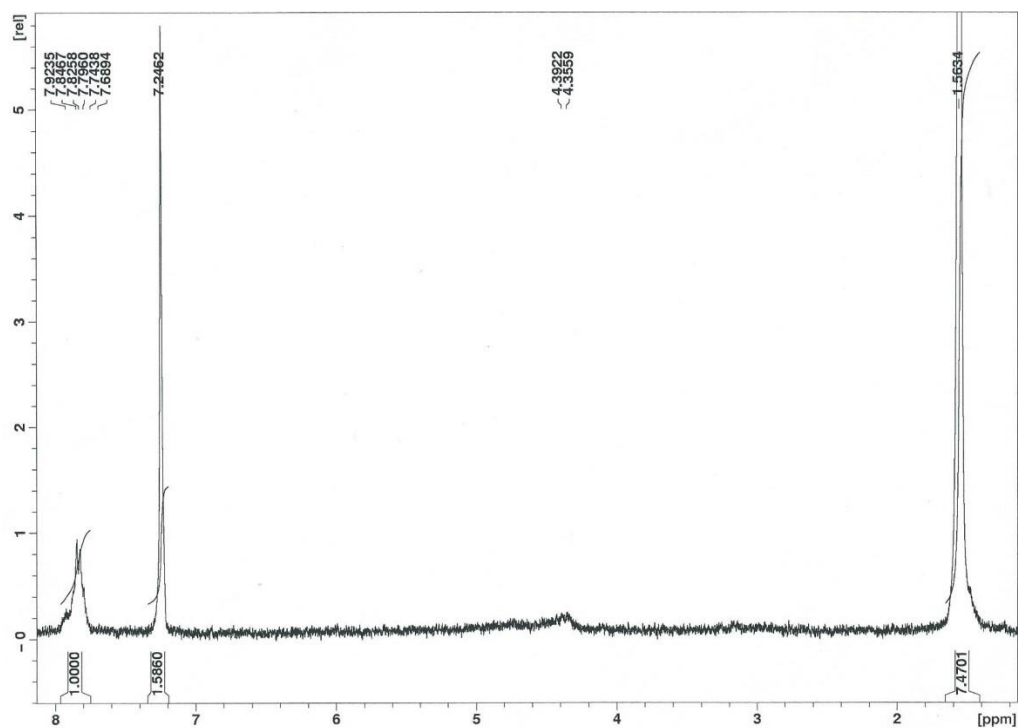


Intermediate (r) was dissolved in dimethylformamide (DMF) (1 mL, 0.5 M) along with 2-bromo-4-chloro-1-iodobenzene (0.04 g, 0.13 mmol). This mixture was degassed for 30 minutes. CuI (0.003 g, 0.014 mmol), cesium(I) fluoride (CsF) (0.04 g, 0.26 mmol), and

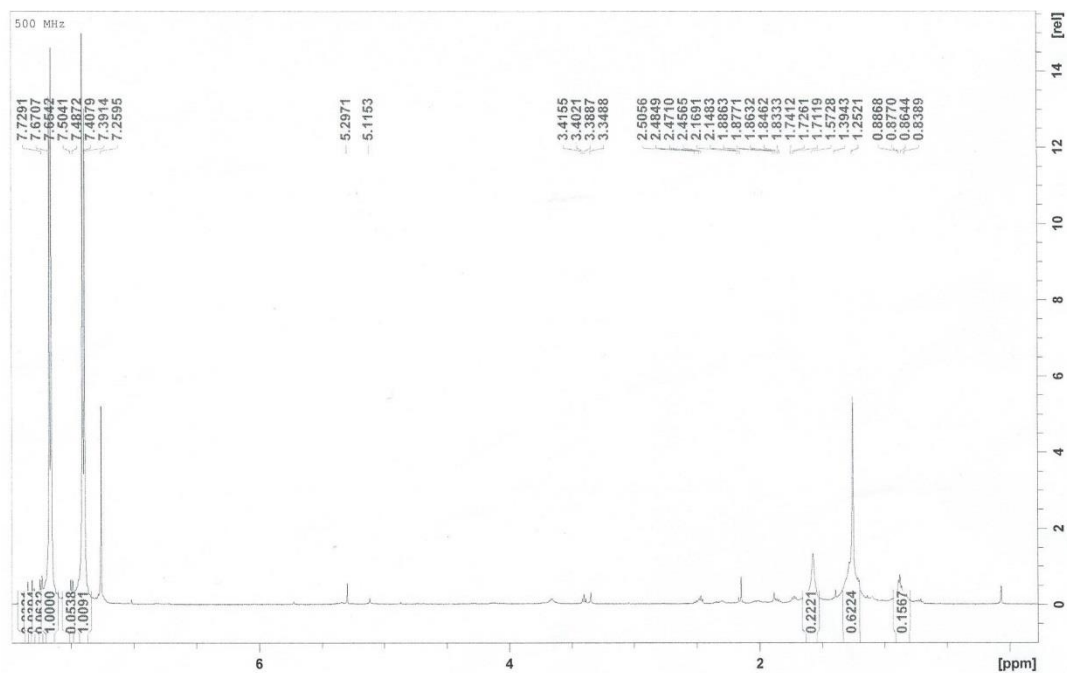
$\text{Pd(PPh}_3)_4$ (0.007 g, 0.006 mmol) were added to the reaction mixture, heated to 60 °C and run for 12 hours. The reaction was monitored by TLC, and filtered through a silicon dioxide (SiO_2) pad with DCM and acetone. The DCM and acetone were evaporated using a rotary evaporator, extracted with DCM and H_2O , and dried with Na_2SO_4 . The crude product was then sent through a plug with 60% DCM:Hx, however no product was present. The reaction was deemed unsuccessful due to lack of appropriate starting material (r).

¹H NMR DATA

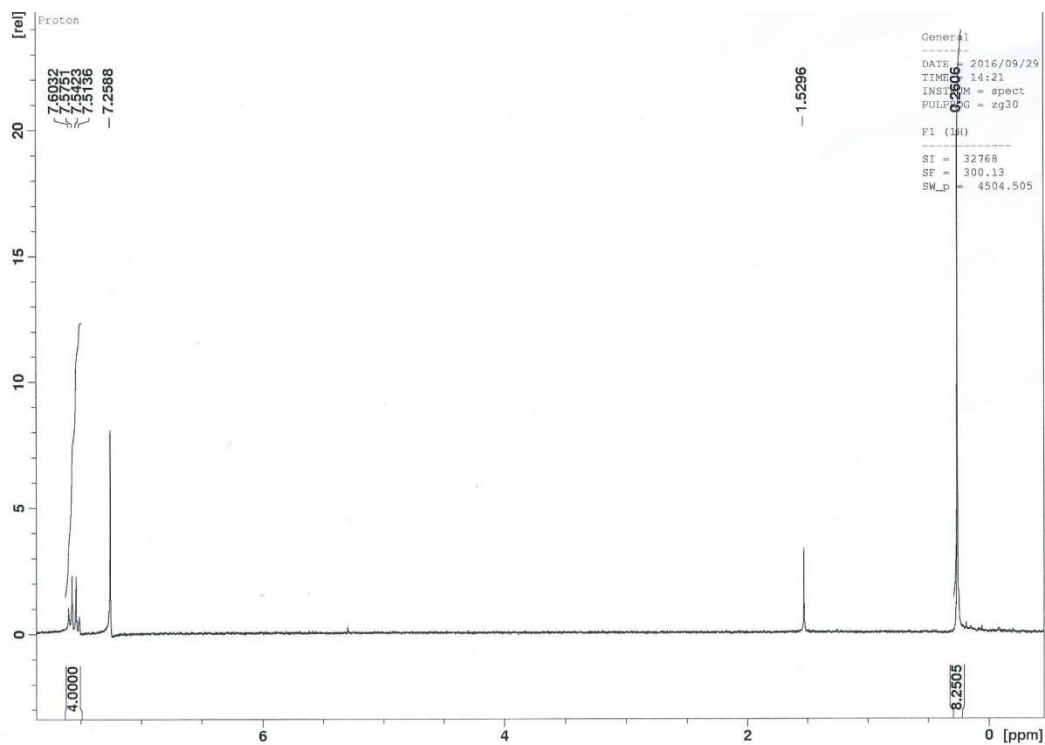
¹H NMR Spectrum for 4,4'-carbonyldibenzonitrile (a):



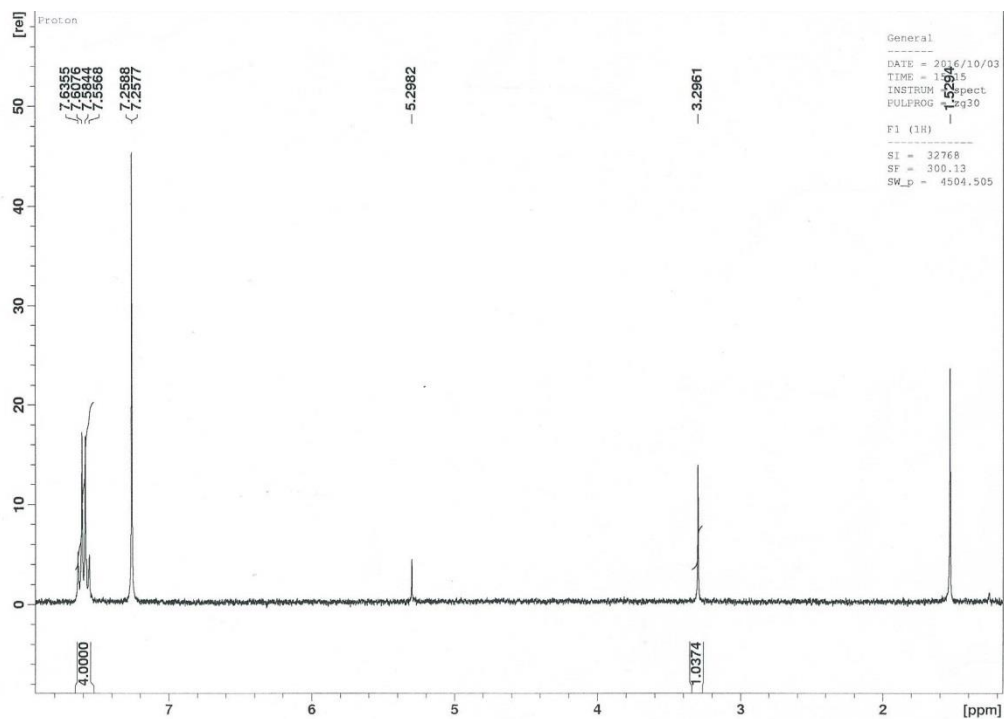
¹H NMR Spectrum for 4,4'-(2,2-dibromoethene-1,1-diyl)dibenzonitrile (b):



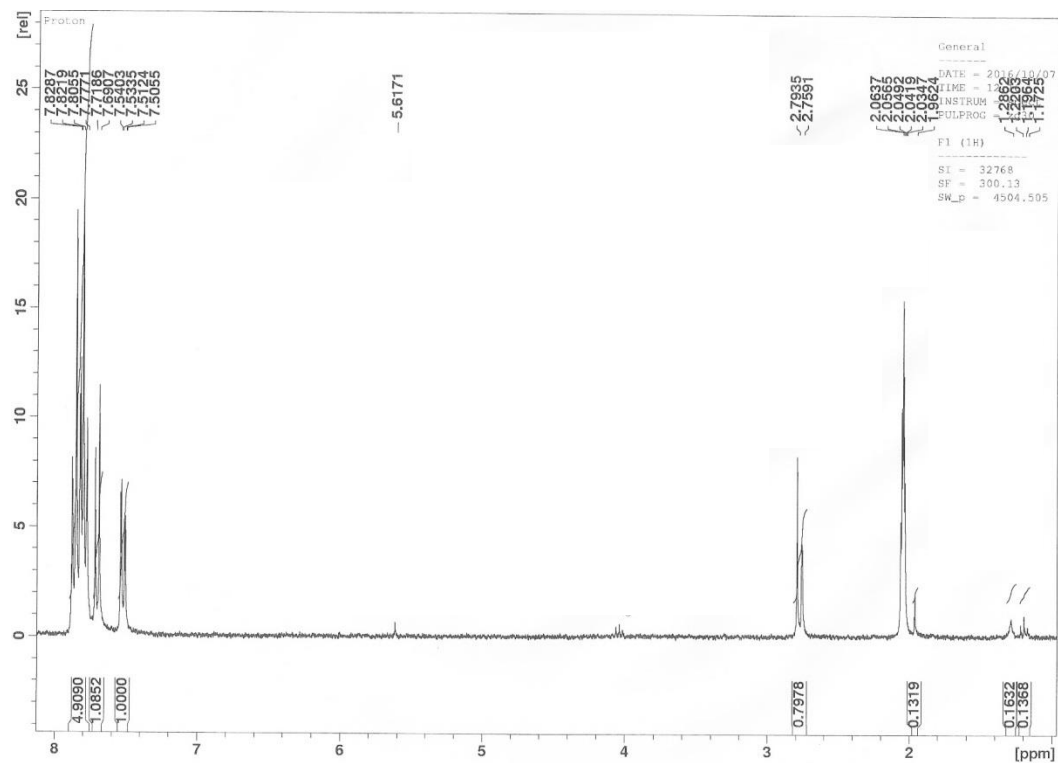
^1H NMR Spectrum for 4-((trimethylsilyl)ethynyl)benzonitrile (n):



^1H NMR Spectrum for 4-ethynylbenzonitrile (o):



¹H NMR Spectrum for 4-((2-bromo-4-chlorophenyl)ethynyl)benzonitrile (p):



¹H NMR Spectrum for 5'-chloro-2'-((4-cyanophenyl)ethynyl)-[1,1'-biphenyl]-3-carbonitrile (q):

